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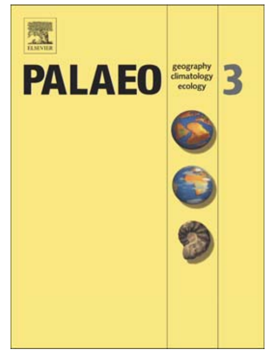

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Depositional environments and diagenesis of a carbonate till from a Quaternary paleoglacier sequence in the Southern Velebit Mountain (Croatia)

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Abstract

Glacial sediment is an important paleoclimatological and paleoenvironmental archive. In the Mediterranean region most of the Quaternary glaciers were hosted in carbonate mountains. Diagenetical processes in carbonate sediments tend to impact preservation of glacial features and complicate the establishment of accurate chronologies. This paper presents a sedimentological study of a paleoglacier hosted in the carbonate Velebit Mountain, Croatia. Three carbonate tills were studied in order to evaluate their depositional environments and the diagenetical processes that affect them. The tills were selected from lateral moraines of different glacial stages of the paleoglacier and they are interpreted as lodgement and melt-out tills. Diagenetical processes such as cementation, dissolution and increase in organic content were enhanced by the percolation of water through the sediment and the propagation of rootlets. This research demonstrates the importance of understanding the diagenetical processes affecting carbonate tills after their sedimentation. Studies like this are an essential research stage prior to conducting geochronological and paleoclimatological interpretations based on paleoglaciers in carbonate regions.

Keywords: Paleoglacier; Till; Carbonate diagenesis; Velebit Mt.; Croatia

1. INTRODUCTION

Mountain glaciers have high climate sensitivity and are ideal records of changes in climate (Owen *et al.*, 2009). In regions where glaciers have disappeared, past climate changes can still be studied using their geomorphological or sedimentological record. Glacial sediments are valuable archives of information used to reconstruct paleoclimate and paleoenvironments (Nesje and Dahl, 2000; Menzies, 2002; Benn and Evans, 2010), but there are deformation (e.g. van der Meer *et al.* 2003; Clarke 2005; Phillips *et al.* 2011) and diagenetic (e.g. van der Meer and Menzies 2011) processes ongoing during and following deposition.

Carbonate rocks are subject to early diagenetic processes such as dissolution or cementation, (e.g., Marshall, 1987; Boggs, 2009). Dissolution occurs when the water percolating through the carbonate sediments is subsaturated in their respective carbonate minerals. Rainwater is subsaturated in carbonate minerals, and the solution gets even more acidic after passing through soils. Therefore, dissolution takes place on exposed sediments and in (or under) soils in contact with non-stagnant water until chemical equilibrium is achieved. Consequently, the dissolution of carbonate particles in sediments could impact the preservation of small-scale glacial features and change properties of the sediment. Glacial striations and other small erosive features are diagnostic evidence for the extent of glaciers in regions that lack other indicators (Reading, 1996; Glasser and Bennet, 2004). Therefore, understanding the preservation potential of small-scale erosive features like these is important in order to consider them reliable indicators of a glacier's extent. Furthermore, change of the sediment properties by diagenetic processes could cause inaccuracy of the chronologies when dating these sediments and paleoclimate interpretations are likely to be compromised. Therefore, in order to avoid this kind of problems it is crucial to understand all the processes affecting these sediments during and after their deposition.

The aim of this study is to characterize glacier sediments from a carbonate region, reconstruct glacier paleoenvironments, and identify diagenetic processes in these deposits. For this purpose, we studied three glacier deposits from Rujno Valley at Velebit Mountain (Croatia). The detailed characterization of these sediments has revealed a variety of diagenetical processes. Therefore, in carbonate regions, studies like the one presented here, are essential for conducting subsequent reliable chronological and paleoclimate studies.

2. REGIONAL SETTING

The study area is located in the southeast sector of Velebit Mountain in Croatia (Fig. 1). This range is 145 km in length along the Adriatic coast and has a maximum elevation of 1757 m asl (above sea level). Velebit Mountain is composed of a sedimentary sequence several thousand meters in thickness ranging from Carboniferous to Tertiary age that was uplifted during the Alpine Orogeny (Vlahović *et al.*, 2005). The predominant lithology in the studied region is Jurassic limestones and dolomites, although limestones, dolomites and carbonate sandstones from the Triassic are also present (Sokač *et al.*, 1967).

The climate in the study area has mountain characteristics. The mean annual precipitation was 1973 mm for the period 1980-2009 in the mountain meteorological station of Zavižan, at 1594 m asl, 60 km north of the study site along the range (Meteorological and Hydrological Service of Croatia; http://www.meteo.hr). Summer is the period of the year receiving less precipitation, although there is no dry season; mean precipitation of the driest month (July) was 68 mm during the reference period. During the same interval, the mean annual temperature was 3.9 °C, with mean minimal temperature of the coolest and warmest months being -4.2 °C (February) and 13.0 °C (July) respectively. Under these climatological conditions there are no modern glaciers on Velebit Mountain.

This research focuses on glacial sediments from Rujno Valley, an intramontane basin in Velebit Mountain (44.36° N, 15.41° E). The valley has a NW-SE orientation and is divided in two sectors, Veliko Rujno to the South and Malo Rujno to the North. A plateau with a mean elevation 1400 m asl extends north of Rujno Valley, whereas south of the valley the mean elevation of the summits is <1000 m asl. The upper parts of Velebit Mountain, including the plateau north of Rujno Valley, hosted glaciers during the Late Quaternary (Nikler, 1973; Belij, 1985; Marjanac and Marjanac, 2004; Bognar and Faivre, 2006; Velić *et al.*, 2011). In the plateau north of Rujno Valley, these glaciers formed an icefield with outlet glaciers flowing down from the highlands. One of these outlet glaciers descended the steep slopes of the plateau towards Malo Rujno forming Rujno paleoglacier (Fig. 1). The mean altitude difference between the current plateau and the valley is 600 m, which should cause temperatures in the valley to be >3 °C higher than in the plateau due to adiabatic changes (e.g., Roedel, 1994). The catchment area of this paleoglacier extends over 19.5 km^2 and is the largest of this sector of Velebit Mountain. The extent of tills in Malo Rujno is limited by the large topographic gradient with the plateau, despite the relatively large accumulation area on the plateau (Fig. 1). Most of the tills preserved in Rujno valley correspond to the left lateral moraine of the outlet paleoglacier. The morphology of the glaciogenic deposits on the right side of the paleoglacier is poorly preserved due to gravitational processes after deglaciation. There is a sequence of alluvial fans and fluvial terraces in connection with different stages of the paleoglacier (indicated by moraines). The study of this sequence is still ongoing. The tills of Rujno paleoglacier reach a minimum altitude of 800 m asl.

3. METHODS

Tills from three locations at Rujno Valley were studied in detail (Fig. 1 and Fig. 2): Jovići Moraine (VR-JM), Rujnička Kosa (VR-RK) and Internal Trench (VR-IT). Trenches up to 3 m in depth and 1 to 4 m in width were excavated or cleared in order to get vertical sections and discern the stratigraphy of the deposits. Sediments were described in the field and sampled for further analysis. Samples of 0.5 to 5 kg were taken for determination of particle-size distribution by sieving, Robinson pipette, and laser diffraction methods. An additional sediment sample of 20 kg from each till was collected for evaluating the organic content. The depositional architecture was described for the sections with non-massive structure.

Textural analyses of the sediments were done by dry sieving after dispersing the cohesive samples with gentle mechanical or chemical processes, taking special caution so that the original grains were not damaged or dissolved. Particles aggregated due to cements accounted in all cases for <5 % of the sample weight. Since these aggregates were present in all sand fractions, they were retrieved by hand from every class in which they were found and from the total weight sum before producing the distributions charts. The sieves used had 32000, 16000, 8000, 4000, 2000, 1000, 500, 212, 106 and 53 μm mesh size and the Robinson Pipette method was used for the 53-20, 20-2 and <2 μm fractions. Additionally, the details in the distribution of particle size for the silt and clay fractions were obtained using a Beckmam Coulter LS 13 320 laser diffraction analyzer. Morphometric parameters from the fraction 212-500 µm were measured using the Morphologi G3 system from Malvern Instruments Ltd coupled with an Olympus BX51M microscope. This technique allowed the calculation of mean grain diameter, elongation (1-width/length), perimeter, circularity ($\sqrt{4 \cdot \pi \cdot area/perimeter^2}$) and convexity (convex hull perimeter/particle perimeter). The mean roundness of particles from this fraction was calculated using the contour images of a population of 100 grains according to Krumbein (1941) comparative charts. In order to study the small-scale erosional features of the gravel-size particles in the tills, some pebbles were collected and wrapped separately to avoid any possible alteration of their surface. The matrix coating of these pebbles was removed by 1) careful rinsing and 2) using an ultrasonic bath. The morphoscopy of pebbles was characterized with low vacuum scanning electron microscope (SEM) and binocular lenses that were used to take images of small-scale erosional features and cements. Furthermore, when possible, samples of undisturbed cohesive sediment were consolidated with epoxy resin and thin sections were done in order to get insight into the fabric of the sediment. The organic content of the sediment was studied in the three sections. Samples were collected in the lower section of the profiles where rootlets were not visible. The sediments were processed according to Newnham *et al*. (2007) and characterized using binocular lenses and SEM. All these laboratory analyses were carried out in the facilities of the Centro Nacional de Investigación sobre la Evolución Humana, Burgos, Spain.

4. RESULTS

4.1. Characterization of tills

Studied tills from Rujno Valley (VR-JM, VR-RK and VR-IT) are from left lateral moraines of the Rujno paleoglacier and correspond to different glacial stages. The most external moraine, corresponding to the earliest identified glacial stage, is the Jovići Moraine. The crest of this moraine can be tracked for over 500 m, and shows an outstanding blunt morphology (Fig. 2). These moraine sediments have an average thickness of 10 m and is overlying previous deposits. There is no trace of proglacial fluvial deposits associated with this till due to erosion or burial during subsequent glacial stages. The studied till of this moraine (VR-JM) is located in the external slope of the moraine (Fig. 1). Rujnička Kosa moraine has the largest preserved crest of Rujno paleoglacier with over 1000 m in length, and its morphology is relatively sharp (Fig. 2). This moraine overlies previous moraines, including Jovići Moraine. The VR-RK till is located in the inner side of the moraine (Fig. 1). The Rujnička Kosa moraine has lateral morphological continuity with an alluvial fan that extends along most of Malo Rujno in the outwash zone of Rujno paleoglacier. The last studied moraine, Internal Trench, is the largest of a series of three recessional moraines within the canyon that connects the plateau and Malo Rujno valley and represents a later stage of the Rujno glacier after the Rujnička Kosa moraine. The crest of this moraine is clearly identified while parallel to the paleoglacier direction, whereas gravitational process affected its preservation when the till descends to the bottom of the valley as a terminal moraine at the snout of the paleoglacier. Where preserved, the crest of the Internal Trench moraine has a sharp morphology similar to the crest of Rujnička Kosa moraine. The VR-IT till section is located in the internal side of the moraine (Fig. 1), in a sector where the crest is not clearly discernible. The Internal Trench moraine has morphological lateral continuity with a terrace incised 2 m in average in the paleo-alluvial fan. The active channel and alluvial plain of the creek that has occasional flow in this valley are dissected in relation to this terrace.

A trench 4 m in width and 3 m in depth was cleared in Jovići Moraine. This section shows a homogenous till unit: VR-JM (Fig. 3). The sediment is massive and predominantly matrix supported. No clear fabric is observed in the general section, although thin sections have revealed that imbrication of elongated granules and pebbles occurs (Fig. 4). The sediment is highly cohesive and cements are rare. However, within the first 0.5 m of the section these properties are disrupted by soil processes. Most of the gravel-size particles have diameters of 3 to 5 cm, although cobbles of 10 to 15 cm in diameter are common (Table 1). Within the studied section two boulders >0.5 m in diameter were found. The average roundness of the pebbles in this till is subangular (Table 2). The sample for lab analyses was taken at a depth of 2.5 m. A pit 2.5 m deep and 1 m wide was excavated in the Rujnička Kosa moraine. This section has a homogeneous till unit: VR-RK. The sediment is massive and clast supported (Fig. 3). No fabric was found in the outcrop and thin sections did not show any fabric either. The sediment is loose, although cohesion of some granules and pebbles occasionally occurs. Thin cements coated some pebbles, although in most cases they were not thick enough to aggregate particles. Most of the gravel-size particles are 1 to 5 cm in diameter, although cobbles 10 to 20 cm are common. In average, the roundness of pebbles and cobbles is subangular. There is a larger variety in the composition of clasts compared to VR-JM, and although Jurassic particles still prevail, Triassic clasts are more common and occasional reworked fluvial Quaternary sediments are found. The sample for laboratory analyses was taken at a depth of 1.8 m. In the studied recessional moraine, a trench 2 m in depth and 3 m in width was cleared. This section is not homogeneous and two units were identified. A sketch of the depositional architecture of this section is shown in Figure 5. The basal unit is composed of a clast-supported till with abundant matrix, alternating with beds of clast supported gravels, where most of the matrix has been washed out. These later beds correspond to channels with variable lateral continuity. Most of the gravel-size particles from this unit are 1 to 3 cm in diameter, although pebbles and cobbles up to 20 cm are common. Some small boulders were also found within the cleared section. The pebbles of this unit are subangular in average, although the pebbles filling the channels are commonly less angular. One small channel (<10 cm in lateral extent) filled with well sorted sand and having parallel stratification was found behind the protection of a large cobble. The VR-IT sample taken for laboratory analyses of this till was taken from a homogeneous sector of the section not affected by channels, at a depth of 1.3 m. Overlying the previous unit is a clast-supported sediment with abundant matrix. The contact with the underlying unit is erosive, and lags of coarse clasts are common at the base and within this unit. The dominant diameter of gravel-size particles is 1 to 5 cm although cobbles and boulders up to 35 cm in diameter are frequent. The rest of sediment properties do not differ from the previous unit. The top of the section has a thick soil layer that prevents a proper characterization of the original sediment.

Textural analyses were carried out in the three studied sediments (Fig. 6). These tills are very to extremely poorly sorted, with two modes in grain size, at the medium-fine pebble and the medium-very fine silt fractions. The largest quantity of slit and clay is recorded in the VR-JM till, which favored the sediment cohesion. On contrast, VR-IT till has the lowest silt and clay content. Statistics of the textural analyses are given in Table 1. The curves of the cumulative particle size distributions show multiple slope changes indicating the occurrence of a variety of processes affecting the till, such as crushing and abrasion (Haldorsen, 1981). The sediment fraction <63 μm (obtained after wet sieving from of an aliquot of the original sample) was analyzed by laser diffraction in order to investigate the detailed particle size distribution of clay and silt in the tills. The three tills show a trimodal distribution with relative particle size maxima at 5 ±2, 16 ±3 and 40±7 μm (Fig. 7). According to this analysis, no major differences exist in the particle size distribution in the clay and silt fraction of the three tills. Morphometric analysis of the 212-500 μm fraction (Table 2) shows that majority of particles have smooth outlined shape features that may be an outcome of incessant shearing (Mahaney, 2002; Altuhafi and Baudet 2011). The study of organic content of the three tills provided notable differences between tills. VR-JM till has a very limited amount of organic content (~1 ppm in weight) that includes palinomorphs and some undifferentiated organic fragments (Fig. 8). On the other hand, the VR-RK and VR-IT have two orders of magnitude higher organic content. Most of the organic content increase is due to rootlets. These rootlets are present in the sediment even if they were not visible during field sampling after careful examination.

4.2. Preservation of erosional features

The gravel-size particles from the Rujno Valley tills display traces of erosion. Selected pebbles were used to characterize their morphoscopy and to identify small-scale glacial erosion features, including striations, polished surfaces and small grooves (Fig. 9). Linear erosional features such as striations and grooves have no predominant orientation on the pebbles and some of them superimpose previous lineaments. They are a few millimeters in length and up to several hundred microns deep. The pebbles often display smooth edges due to erosion that increases the roundness of the particles. The preservation of these erosional traces is compromised by dissolution features that have different evolutionary stages. The initial corrosion features, characterized by dissolution pits, are preferentially located on rougher surfaces such as those found on grooves (Fig. 9 and Fig. 10). Advanced corrosion in pebbles may prevent the identification of any glacial erosion feature, and differential weathering up to 5 mm has been observed in some cases. This advanced corrosion is common along the edges of pebbles, although in some clasts the whole surface is affected. The variability in the carbonate lithology did not appear to cause the different degrees of corrosion in gravel-size particles. In addition to the dissolution features, these sediments have occasional cements (Fig. 10). Small-scale glacial erosion features are not found in gravel-size particles exposed to the surface due to active dissolution processes (Krklec, 2011).

Pebbles from the Jovići Moraine till display well preserved small-scale glacial erosion features. Traces of corrosion in this sediment are rare. The top of the largest boulder in this section shows up to 3 mm of differential weathering. A fracture along which water percolates is likely to be the cause of the observed local corrosion process. The preservation of glacial erosion features in pebbles from Rujnička Kosa till is variable. The distribution of corrosion in this till is widespread and it is common to observe single pebbles with both deep corrosion and well preserved erosional features. Occasionally, carbonates precipitate as thin film cements on the pebbles, although rhizoliths are also observed (Fig. 10).

The lowest preservation of small-scale glacial erosion features is found in the pebbles from the Internal Trench till and pebbles with their whole surface affected by corrosion are frequent. Despite the greater porosity of this till, occasional cements do not compromise the loose nature of most of the sediment. Thicker film cements are observed in this till and rhizoliths are common. Some of the pebbles have carbonate cements coating the downside facet of the pebble whereas their upside surface display traces of heavy weathering.

5. DISCUSSION

5.1. Environmental reconstruction

The Equilibrium Line Altitude (ELA) is the elevation that divides the glacier ablation and accumulation zones (e.g., Oerlemans, 2010). During the Last Glacial Maximum (LGM), the ELA in Velebit Mountain has been estimated to be in an elevation range of 1217-1300 m asl (Belij, 1985; Bognar and Faivre, 2006) based on Höfer's method of snow-line determination (Höfer von Heimhalt, 1879). Despite more accurate methods to calculate paleo-ELAs (Nesje, 2007), this reported value for the ELA during the LGM is in agreement with regional paleo-ELAs modeling (Allen *et al.*, 2008). The relative accuracy of these results is confirmed by regional studies of paleo-ELAs during the LGM in mountain paleoglaciers of southern Europe, at comparable latitudes (<4° difference) and with a similar climate context, and are in an elevation range of 1300-1750 m asl (e.g., Kuhlemann *et al.*, 2008; Vieira *et al.*, 2008; Milivojević *et al.*, 2008; Cowton *et al.*, 2009; Giraudi, 2011). The plateau of Velebit Mountain (average elevation 1400 m asl) and the Malo Rujno intermontane depression (average elevation 800 m asl) are connected by a high gradient slope dissected by the Ribnička Vrata Canyon. During the LGM, the ELA of Rujno glacier was likely located between the upper sector of the Ribnička Vrata Canyon and the edge of the Velebit Mountain plateau facing Malo Rujno. Thus, the outlet glacier reaching the Rujno basin was located in the ablation zone of the glacier with temperatures several degrees higher than in the plateau due to the adiabatic thermal gradient. Under these conditions the glacier had limited extent along Malo Rujno before its complete melting. Although lower ELAs could be found in glaciations previous to the LGM, geomorphological evidence of Middle Pleistocene glaciations in other Mediterranean mountains suggest that differences were limited (e.g., Gianotti *et al.*, 2008; Delmas *et al.*, 2011). However, paleo-ELAs in some regions of Dinarides are controversial due to possible misinterpretation of glacier extensions and their chronology (Milivojević *et al.*, 2008; Hughes *et al.*, 2010, 2011; Djurović, 2012; Domínguez-Villar *et al.*, 2013).The sequence of moraines observed in Malo Rujno represent the terminal deposits of a series of glacier stages where the left lateral moraines, and in some cases their proglacial outwash deposits have been recorded. This morphostratigraphical evidence supports similar paleo-ELAs during different stages of Rujno paleoglacier in agreement with other Mediterranean sites (e.g., Gianotti *et al.*, 2008; Delmas *et al.*, 2011). This paleoenvironmental reconstruction modifies previous interpretations of these sequences that suggested the Rujno tills could be medial moraines of larger glaciers (Marjanac and Marjanac, 2004; Marjanac, 2012).

Beyond the general picture obtained by the geomorphological setting of the glacial record, the study of the sedimentology of three tills may provide additional paleoenvironmental information for these moraines. The high degree of compaction in the till studied in Jovići Moraine, together with the large proportion of silt and clay, the extremely poorly sorted nature of the sediment and the deformation fabrics observed in some of their particles indicate that this is a lodgement till (subglacial traction till *sensu* Evans et al., 2006). This till was deposited at the base of the glacier, although currently the outcrop is at the surface of a lateral moraine in a relatively elevated position. The location of the deposit within the moraine and the blunt morphology of the crest of the moraine suggest that this moraine has been subject to substantial erosion and that the morphostratigraphical sequence of this moraine could be incomplete. The till studied in Rujnička Kosa moraine has substantially less silt and clay compared to VR-JM. This sediment is massive, clast supported, extremely poorly sorted, without any deformational fabric and is located in the internal side of a lateral moraine. We interpret this sediment as a melt-out till and based on its location proximal to the moraine crest, together with the absence of any evidence of running water, we speculate that it could represent a supraglacial environment. Finally, the section studied in the Internal Trench moraine has two different units. The studied sample from VR-IT till has the lowest amount of silt and clay, is clast supported, very poorly sorted, although laterally, channels of clast supported pebbles or well sorted sand provide evidence for the flow of water. This unit has been interpreted as a subglacial melt-out till with channels draining the melt water from the glacier. The overlaying unit displays sediments with relatively similar characteristics to VR-IT, although the difference is that the unit is not massive and several lags have been identified at the base and within the deposit. Considering the morphostratigraphical position of the till, where the crest of this moraine has not been preserved likely due to the collapse of part of the sediment after the glacier retreat, we speculate that this unit corresponds to a reorganization of a melt-out till due to paraglacial processes related to gravitation (Ballantyne, 2002).

5.2. Early diagenetical processes

The three tills display cementation and dissolution processes that have occurred since their deposition. The rare to infrequent occurrence of cements in the three deposits indicates that this is not a major diagenetic process in these sediments. However, evaluating the degree of dissolution in sediments is more complex due to the erosive nature of this process. In this case we assess the importance of the early stages of dissolution by the preservation of small-scale glacial erosive features such as striations, grooves or polished surfaces. The better preservation of micro-scale glacial erosion features takes place in the VR-JM till, whereas the worst occurs in the VR-IT sample. These two samples have the largest and lowest amount of silt and clay respectively. The coating of gravel-size particles by these fine particles prevents their contact with percolating water and then the corrosion of their surfaces by solutions subsaturated in carbonates. This kind of isolation of the larger clasts of the till by the fine matrix permitted the preservation of the small-scale erosional features. The observation of the sediment sections after rain events has shown that after the clearing of profiles, the VR-JM till was dry aside from fractures and the topmost sectors affected by the soil, whereas the VR-RK and VR-IT tills were wet, indicating that the matrix was permeable. Thus, while the preservation of small-scale glacial erosion features is widespread in the VR-JM till, they depend on the particular distribution of a fine matrix around gravel-size particles in the VR-RK and VR-IT tills. As the amount of clay and silt is lower in the VR-IT till than in the other tills, the preservation of erosion features in the pebbles of this sediment was less common.

Carbonate rocks and sediments are subject to dissolution in most surficial and vadose environments (e.g., Ford and Williams, 2007). Regional studies on carbonate corrosion have shown weathering rates on the order of 1.5-7 mm/ka in surface environments whereas subsurface rates >10 mm/ka have been recorded in some cases (Pahernik, 1998; Perica 1998; Perica and Orešić, 1999; Krklec, 2011; Krklec *et al.*, 2013). Under these weathering rates, no small-scale glacial erosion feature on carbonate rocks could have been preserved since the LGM, unless they were isolated from the natural corrosive environment. Most of the well preserved glacial erosive features that we found in the studied pebbles are <0.5 mm in depth. Consequently, their preservation potential in a corrosive environment is less than some centuries after deglaciation. This indicates that the coating of pebbles by the fine matrix has been an effective isolator of these clasts to corrosive percolating solutions. Therefore, in order to determine that small-scale erosive features in carbonate clasts (or eroded rock surfaces), were caused by glacier erosion, their preservation potential according to the sediment properties should be considered to avoid confusion with linear dissolution features (e.g., Ford and Williams, 2007).

Film cements are present in the three tills, although rhizoliths are only observed in the VR-RK and VR-IT tills. The coating cements of the VR-JM till are likely to result from water trapped within the pores of the sediment, since no percolating water affects this till. In the other two tills, we cannot discard an alternative possibility: the film cements could be the result of the percolating water. The occurrence of cementation and corrosion on the same pebble has been observed in the VR-IT till, which is evidence of at least two diagenetical stages with solutions with different saturation in relation to carbonates (e.g., melt water trapped in the sediment and percolating water). However, micro-environmental differences affecting the carbonate saturation index of percolating solutions cannot be completely ruled out as an alternative explanation. This might be supported by observations of preferential cementation concentrated under VR-IT pebbles and cobbles. The VR-RK and VR-IT tills have larger mean grain-size and are less compact than the VR-JM. The roots penetrated in these two tills to depths >2 m and occasionally formed rhizoliths favored by the local impact of the plants in the solution saturation index (Košir, 2004). Although rhizoliths indicate the presence of rootlets in the past (Alonso-Zarza and Wright, 2010), visual inspection and the concentration procedure of organic matter in both sediments have shown that both locations have current rootlets at the depths of sampled sediments. The penetration of rootlets in VR-RK and VR-IT implies an increase in organic content of the sediment. Concentration of organic particles from VR-JM suggests that Rujno tills contain a limited but recordable amount of organic particles in the primary sediment. This includes palinomorphs and other unclassified organic particles. The much higher amount of organic particles (dominated by rootlets) found in VR-RK and VR-IT tills are the clear indicator of organic enrichment by postdepositional processes. However, particles other than rootlets are also likely to be accumulated using the bioturbation space left by roots after their decomposition.

The percolation of rain water through the sediment has been observed in situ in the VR-RK and VR-IT tills. Laser diffraction analyses were conducted in the clay and silt fractions of the three tills to evaluate whether leaching or accumulation of these particles could occur as a result of the percolation, impacting the original properties of the sediment. We use the sample VR-JM as reference, since no percolation takes place in this sediment and these processes affecting the redistribution of clay and silt particles may be discounted. However, as the depositional environments differ, some variability is expected. The results from the laser diffraction (Fig. 7) show that the three tills have three main subpopulations with similar particle diameters centered at 5 ±2, 16 ±3 and 40 ±7 μm. Samples VR-RK and VR-IT do not have particles from different grain sizes and the distribution of the fine sediments is not substantially different to identify any redistribution of the silt and clay fractions. Therefore, we assume that the studied sediments preserve their original textural properties.

5.3. Implications for geochronological studies

The diagenetical processes described in this study (cementation, dissolution and increase of organic content) changed the properties of the sediment and affected preservation of small-scale erosional features (including striations, polished surfaces and small grooves). These postdepositional changes may impact the accuracy of dates produced by different dating methods. This study has identified substantial erosion of Jovići Moraine (>1-3 m), potentially limiting the accuracy of geochronological studies based on terrestrial *in situ* cosmogenic nuclides such as ^{36}Cl. However, this technique was applied successfully in regions where the original morphology of the moraine has not been substantially eroded (e.g., Sarıkaya et al., 2014). Increase of organic matter in the sediments of VR-RK and VR-IT implies that radiocarbon dating is not recommended in order to achieve accurate chronologies of the timing of sedimentation, regardless if the samples are taken as bulk sediment, selected organic fragments or concentration of pollen grains. However, in the case of findings of trunks or other clearly identified non-root fragments, accurate chronological results might be achieved

(Giraudi and Frezzotti, 1997; Monegato, et al., 2007). Radiocarbon analyses from calcite cements are known to be inaccurate due to the dead-carbon contribution from dissolved carbon of the bedrock carbonates (Genty and Massault, 1997) and are not recommended in this context. The use of U-series disequilibrium methods for the dating carbonate cements is generally not used for dating glacial deposits since: (1) cements generally have several phases of growth ranging from the time of deposition to present and (2) more importantly, a closed carbonate system is unlikely to be preserved, implying isotopic leaching and violation of one of the principles of this method (Edwards et al., 1987). Other dating methods such as OSL are not applicable to these glacier sediments, in part due to their lack of exposure to sun light according to the depositional environment described, but more importantly because of the lack of significant amounts of quartz and feldspars in the bedrock carbonates.

This study has shown the importance that some diagenetical processes have in altering the primary properties of the tills. Thus, these sediment modifications might have major implications in the dating of glacial records, preventing accurate regional paleoclimate interpretations (as pointed out by Domínguez-Villar *et al*., 2013). Therefore, geochronological studies in these deposits should take into consideration these postdepositional modifications in order to produce inaccurate chronologies.

6. CONCLUSIONS

The morphostratigraphic and sedimentological study of tills from Rujno Valley presented here allowed the identification of depositional environments of terminal sequences of Rujno paleoglacier and its diagenetical processes. Based on the geomorphological setting and the sedimentological analysis of the glacial sediments from Rujno Valley, lodgement (VR-JM) and melt-out (VR-RK and VR-IT) tills have been identified in three different left lateral moraines along the outlet of Rujno paleoglacier.

Rujnička Kosa and Internal Trench melt-out tills are affected by diagenetical processes such as cementation, dissolution and the increase in organic content (mostly by the incorporation of rootlets), although no sediment leaching was identified in despite of water percolation. In contrast, sediment properties of Jovići Moraine lodgement till such as its high degree of compaction, high proportion of silt+clay fractions and the lack of permeability through the matrix, prevents the water flow through the matrix and the original properties of the sediment are preserved away from the fissure-permeable fractures. These diagenetical features are of importance for geochronological studies. Therefore, in order to conduct reliable paleoclimate or paleoenvironmental evolution studies based on paleoglaciers in carbonate regions, careful studies like the one here presented, are an essential initial research stage that should be carried out.

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Table 1. Statistics of grain size distributions of glacier sediments from Rujno Valley.

Parameter*	VR-JM	VR-RK	VR-IT
Mean (μm)	271	947	2372
	(Medium sand)	(Coarse sand)	(Very fine gravel)
Sorting	24.97	20.24	9.606
	(Extremely poorly sorted)	(Extremely poorly sorted)	(Very poorly sorted)
Skewness	-0.279	-0.487	-0.387
	(Fine skewed)	(Very fine skewed)	(Very fine skewed)
Kurtosis	0.604	0.982	1.113
	(Very platykurtic)	(Mesokurtic)	(Leptokurtic)

* according to Folk and Ward, 1957

Table 2. Bidemensional morphologic parameters of the sand fraction 212-500 μm in glacier sediments from Rujno Valley.

Parameter	VR-JM	VR-RK	VR-IT
Particles (n)	461	440	286
Diameter	345.080 ±78.411	344.679 ±86.707	396.681 ±111.587
Elongation	0.247 ±0.114	0.242 ±0.116	0.263 ±0.132
Perimeter	1174.041 ±281.554	1213.410 ±313.732	1388.090 ±419.308
Circularity	0.923 ±0.032	0.892 ±0.045	0.900 ±0.040
Convexity	0.987 ±0.013	0.965 ±0.029	0.978 ±0.018
Roundness*	0.47 ±0.10	0.34 ±0.11	0.38 ±0.10

* Roundness was calculated for 100 random particles within each sample according to Pettijohn, 1957.

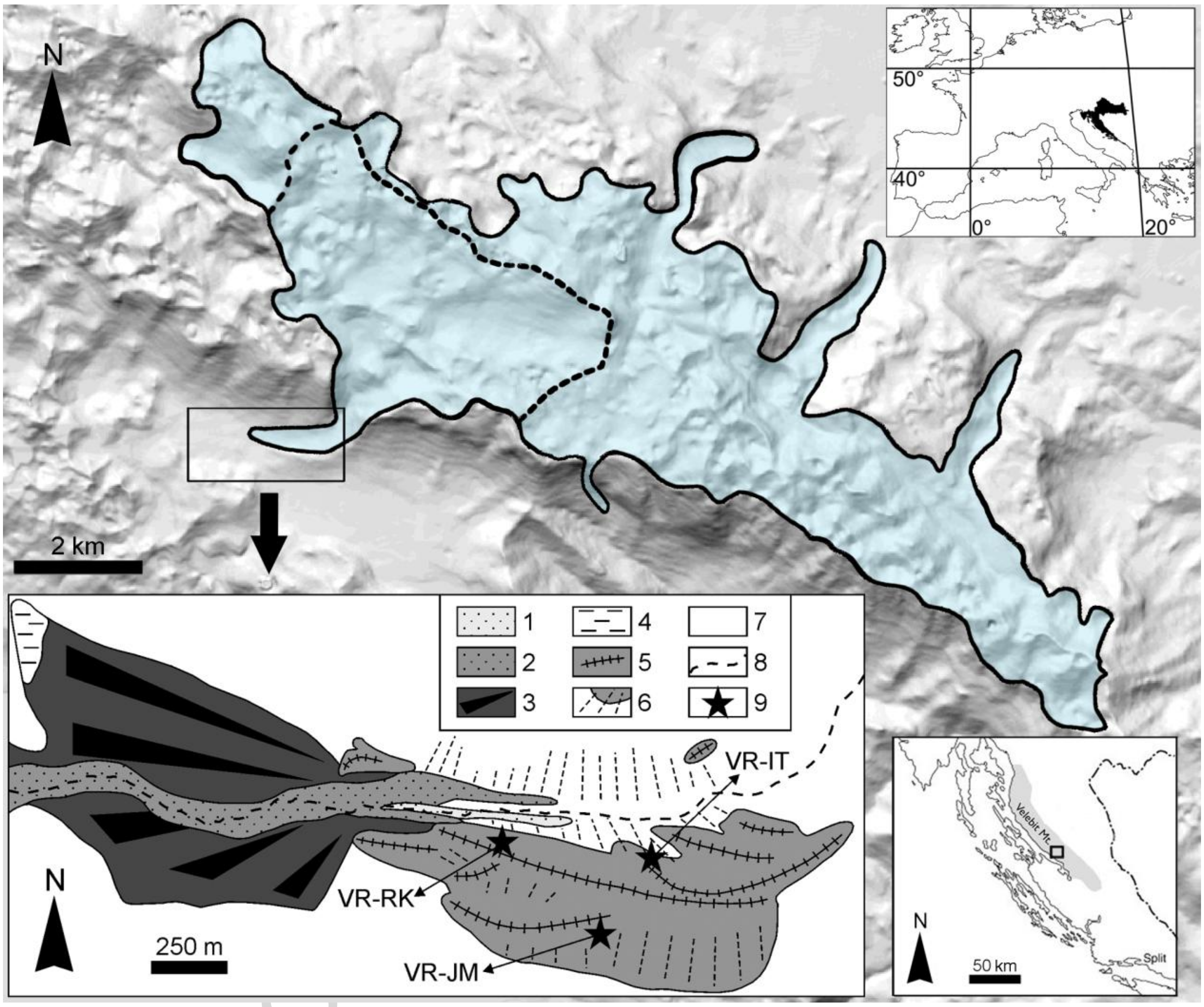

Fig. 1. Digital elevation model of the SE sector of Velebit Mountain, with a tentative outline of the Southern Velebit Icefield. The discontinuous line shows the outline of the area contributing to Rujno Paleoglacier. The location of Velebit Mountain in Croatia is shown in the upper-right inset. A lower-left inset shows a geomorphologic sketch of the study area: 1 Recent/active fluvial deposit; 2 Fluvial terrace; 3 Outwash deposit; 4 Endorheic depression; 5 Moraine crest; 6 Till affected by gravitational processes; 7 Slope; 8 Creek; 9 Study sites.

Fig. 2. Moraines of Rujno paleoglacier: A) General perspective of the Rujno paleoglacier till sequence at Rujno Valley. Moraines studied are Internal Trench (IT), Rujnička Kosa (RK) and Jovići Moraine (JM); B) Blunt crest of JM. The picture is taken from the crest; C) Relative sharp crests of RK and IT moraines.

Fig. 3. Cleared sections of three studied tills: A) homogenous, massive, matrix supported till unit of Jovići Moraine; the scale is 1 m in length. The upper 0.5 m of the section are sediments mobilized decades ago when the pit was originally excavated. B) Massive, clast supported, homogeneous till of Rujnička Kosa moraine. The scale is 1.8 m in length. C) Internal Trench moraine till with two identified units, see figure 5 for stratigraphy details. The trench is 2 m in height.

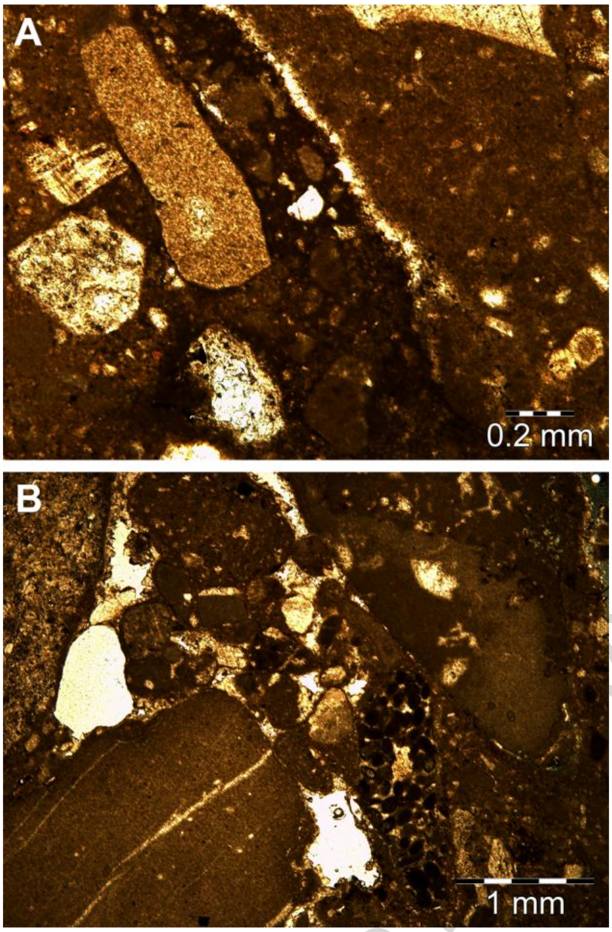

Fig. 4. Thin sections of consolidated tills from Rujno paleoglacier. A) JV-JM till showing fabric with parallel orientation of elongated clasts. B) VR-RK till showing lack of any preferential orientation of clasts.

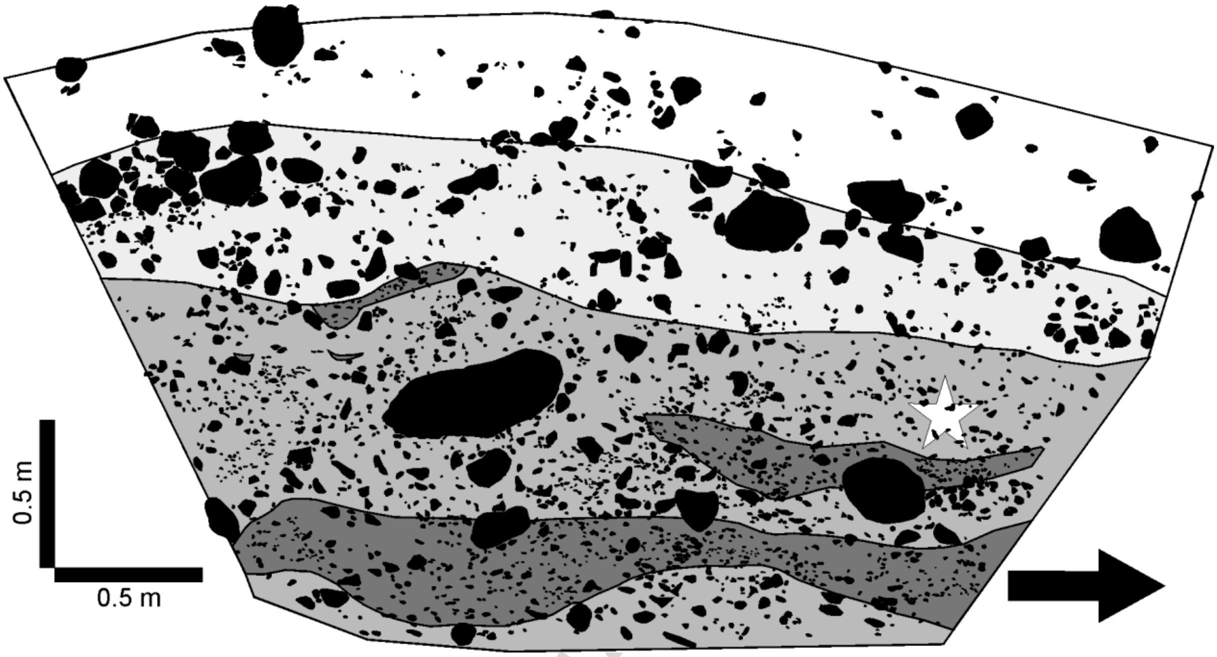

Fig. 5. Depositional architecture of the studied section in the Internal Trench moraine. Visible particles larger than pebble size are coloured in black, while medium and dark grey shading constitute the basal unit (dark grey represent the channel fills). The light gray shading designates the upper unit, whereas the white shading illustrates the section where the soil processes greatly disturb the original sediment. Star marks sediment sample location, while the arrow indicates the glacier paleoflow.

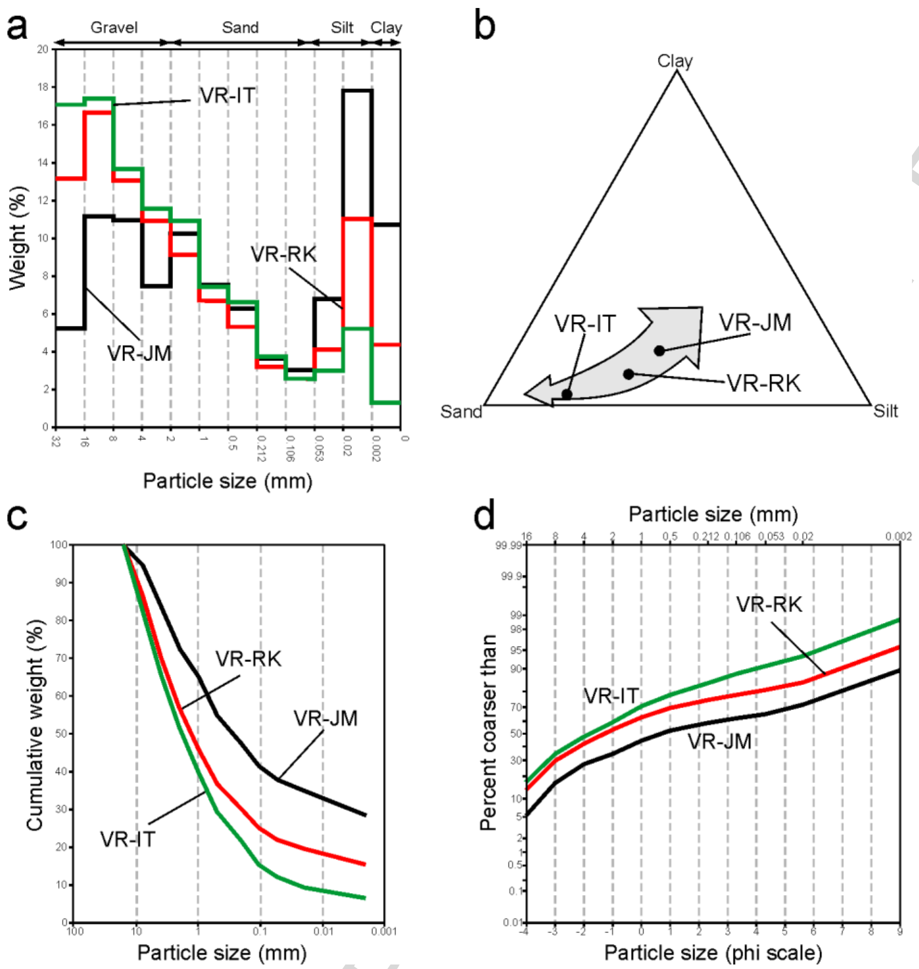

Fig. 6. Textural analyses of VR-JM, VR-RK and VR-IT tills. A) Particle size distributions. B) Ternary graph of the fraction <2 mm. The grey arrow indicates the general range of particle distributions in tills (after Mills, 1977). C) Cumulative particle size distribution curves. D) Cumulative particle size distribution curves in Rosin's law probability graph.

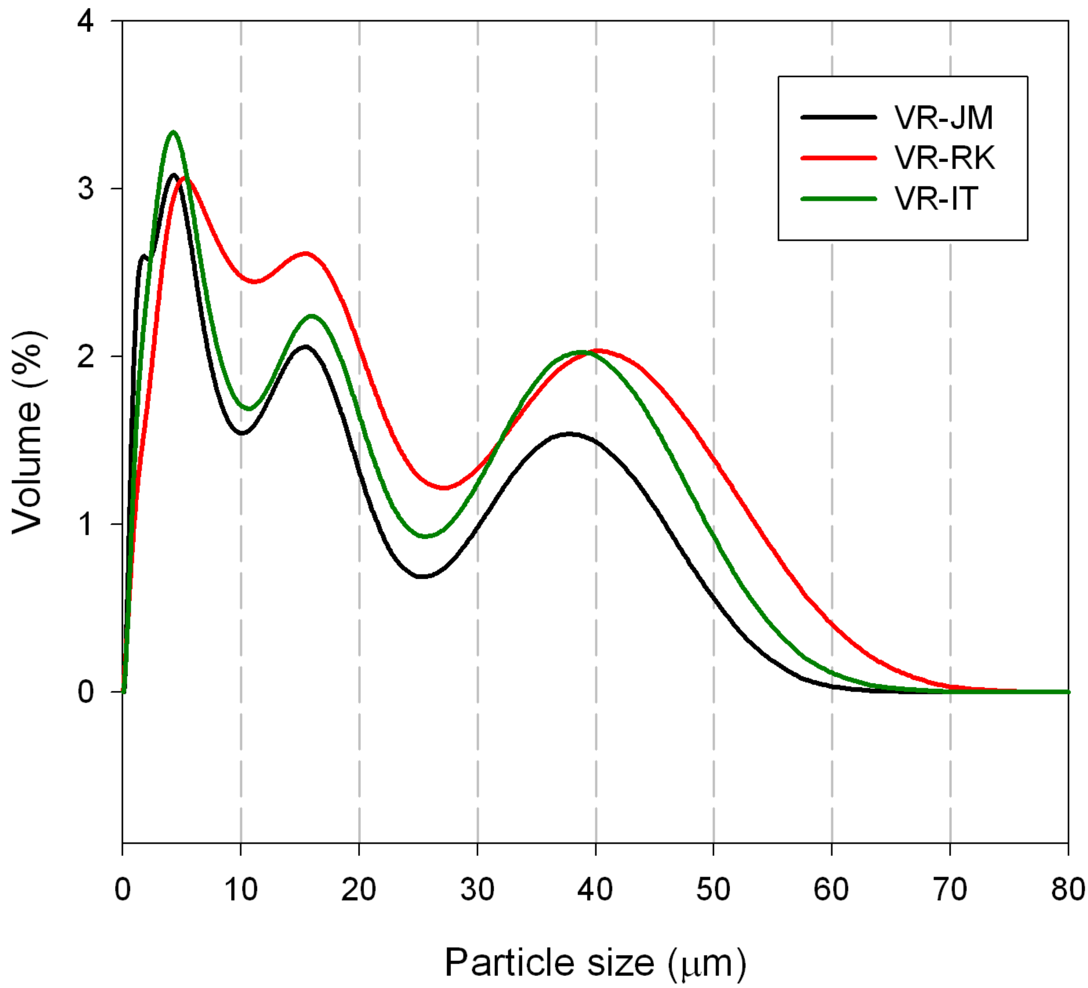

Fig. 7. Particle size distribution curves of the sediment fraction <63 μm of VR-JM, VR-RK and VR-IT tills obtained by laser diffraction.

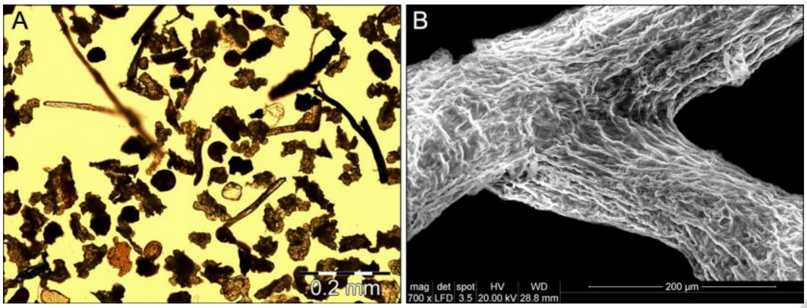

Fig. 8. Organic matter from Rujno paleoglacier tills. A) Image taken under binocular lenses of a subsample from VR-JM till showing the appearance of the organic content. This organic matter is interpreted as particles deposited during till sedimentation. B) Scanning electron microscope image of one of the rootlet fragments from VR-IT that composes most of the organic material from this till.

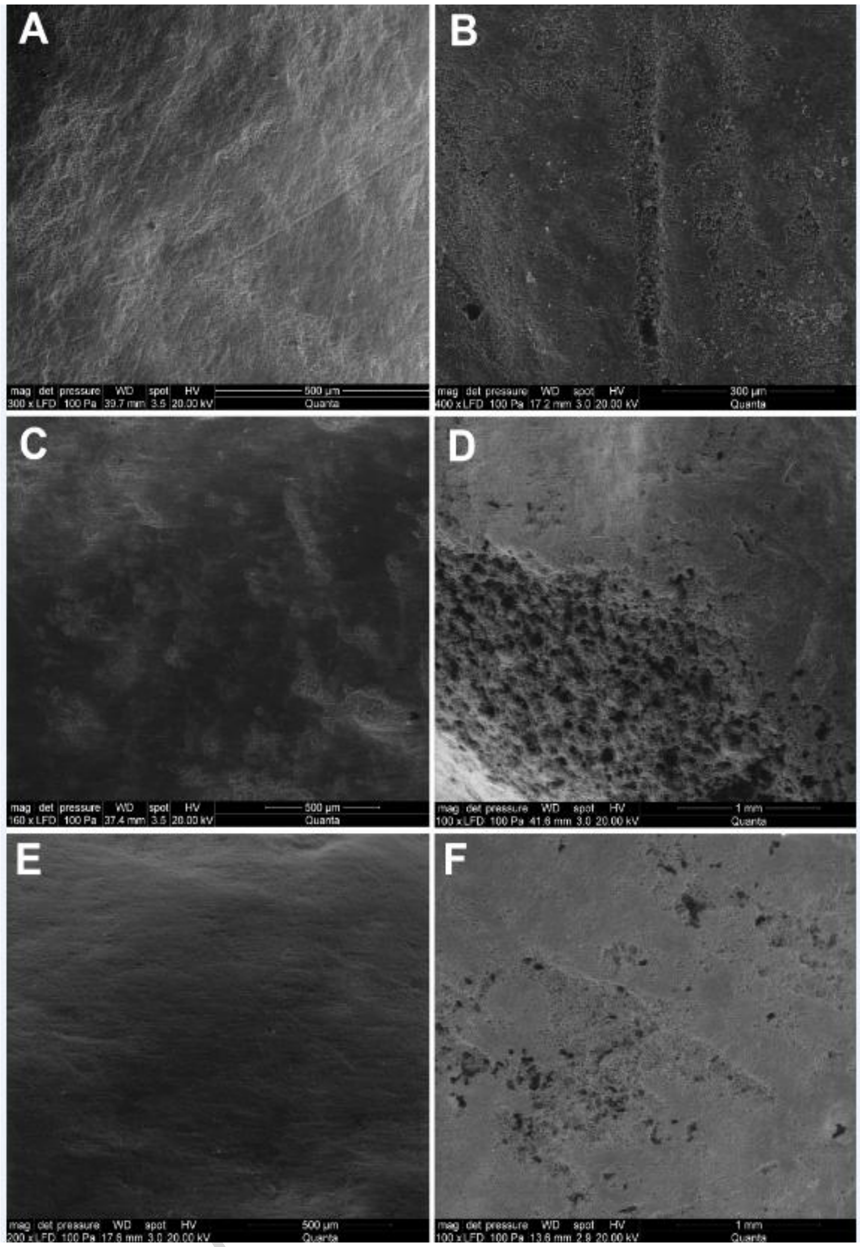

Fig. 9. Scanning electron microscope images of pebbles from Rujno paleoglacier tills. A) Striations from VRJM. B) Grooves from VR-IT. C) Polished surface from VR-RK. D) Pebble edge heavily weathered by dissolution pits in VR-RK. E) Smooth surface of a regular pebble from VR-JM showing the lack of dissolution features. F) Pebble surface with dissolution pits from VR-IT. In this case the dissolution is in an early stage since corrosion has not erased the traces of a groove.

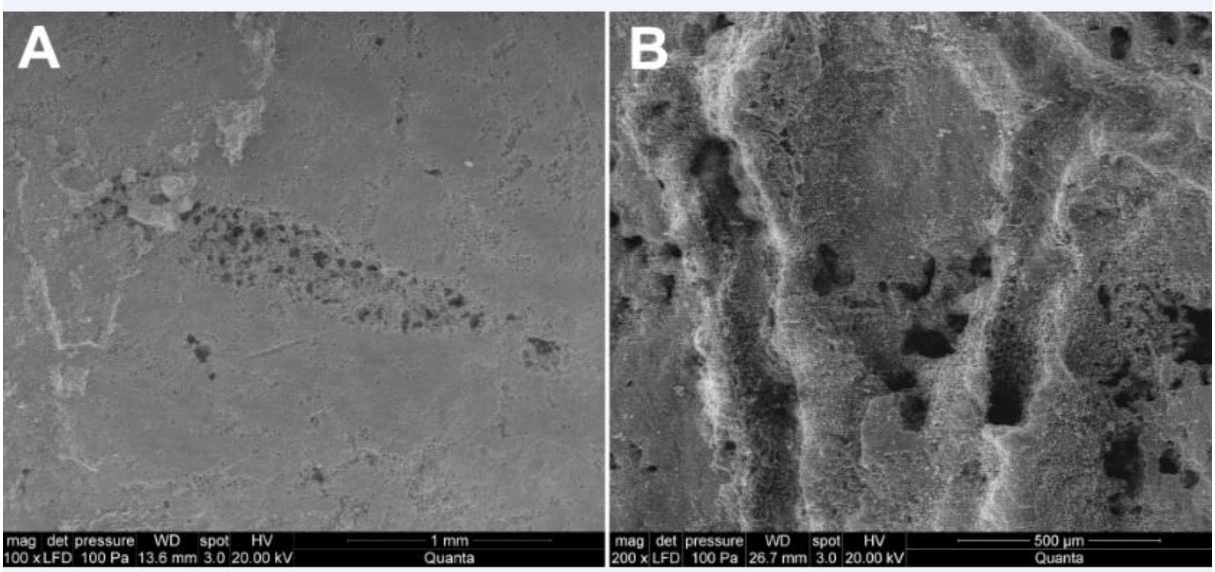

Fig. 10. Scanning electron microscope images of cements. A) Thin peculiar cement partially covering a pitted groove in VR-IT. B) Rhizoliths coating a pebble in VR-RK.

Highlights:

Diagenesis of carbonate tills affects the original properties of glacial sediments.

Dissolution and formation of cements are common processes of early diagenesis.

Dating of carbonate tills by different methods is potentially impacted by diagenesis.